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CORROSION INHIBITION FOR FLOWING STEAM AND CONDENSATE LINES

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8 Claims. (Cl. 252—392)

The present invention relates to processes and compositions for controlling corrosion in flowing steam and condensate lines and particularly for avoiding or reducing the extent of degradation in long straight chain amines.

For some years long straight chain filming amines (U.S. Patent 2,460,259) have been used to inhibit corrosion in condensate return lines, steam lines, dryers, and other post boiler equipment, all of which use flowing water or steam. Excellent inhibition of corrosion has been attained by these materials, but in many cases the amine has degraded to a reddish-brown sludge which tends to deposit in the lines and therefore a great deal of maintenance is required to keep the lines free.

The purpose of the invention is to provide an improved corrosion inhibitor for flowing steam and condensate lines, which will minimize the tendency to degrade of the long straight chain amines now in use.

An extensive research program has been carried out to determine the tendency of various long straight chain amines to degrade. Table I indicates some of the results obtained in this connection. Twenty grams of each amine to be tested was placed in an oven maintained at 400 degrees F. for 5 hours. At the end of this period of test the separate samples were removed from the oven. The appearance of the samples was noted and an infrared spectrogram was run on each sample. The band at about 6.1 microns in the spectrogram is normally present in undegraded amines of this character only in trace amounts. The same is true of undegraded amine-adducts.

By comparing the absorbance of the 6.1 band to the absorbance of the CH_2 groups at 6.8 microns, a relationship for undegraded amines was established.

After heating, the absorbance at 6.1 microns was again measured and compared to the absorbance of the CH_2 band. This comparison of results before and after heating serves as a measure of the degradation.

Thus Table I shows for each amine tested a figure for this absorbance ratio before heating, another figure for the ratio after heating, and a difference corresponding to the amount of degradation.

The exact mechanism of the degradation process is not known to me, but it is commonly believed by authorities in this field to be an oxidation reaction which centers on the amine group. Based on evidence found in our own laboratory, however, it appears that reduction is the basic reaction. This is confirmed by the fact that the degraded amine has an absorption band in the infrared absorption spectrum where the aldehyde group is known to absorb.

When the amines referred to in Table I were tested for degradation tendencies by the measurement of the ratio of amide to CH_2 as above explained, it was noted that the amount of amine which degraded appears to increase

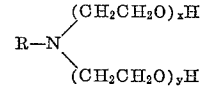
as the amine type varies from primary amine in Experiment 1 to secondary amine in Experiments 2 and 3 and to tertiary amine in Experiments 4 and 5.

It is, therefore, very surprising to find that the formation of tertiary amine by alkyloxylation in accordance with the present invention greatly increases the resistance to degradation rather than reducing it as with ordinary tertiary amines.

Table I shows that the degradation of ethyloxylated or propyloxylated amines was considerably less than that of other tertiary amines and was markedly less than that of primary or secondary amines.

This behavior was observed with carbon chain lengths of from 8 to 22 carbon atoms, and included both saturated and unsaturated amines.

The structural formula of the ethyloxylated amines is shown below:



where:

R is a straight carbon chain from 8 to 22 carbon atoms long
x is an integer from 1 to 25
y is an integer from 1 to 25

The formula for the propyloxylated amine is the same except for the substitution of propyloxylated groups ($CH_2CH_2CH_2O$) in place of the ethyloxyl (CH_2CH_2O).

Having found that alkyloxylation greatly decreases degradation, the alkyloxylated amines were tested to determine whether they are capable of inhibiting corrosion in a simulated condensate system. In the test the effectiveness of the treatment to inhibit corrosion on low carbon steel specimens of the character of AISI 1010 was measured. A simulated condensate was prepared from demineralized water containing 150 p.p.m. of carbon dioxide and less than 0.1 p.p.m. of oxygen. This water was heated to 195 degrees F. and was circulated over the four steel specimens in the system in series at a flow rate of 0.35 foot per second. Weight losses sustained by the specimens when exposed to the condensate water both untreated and treated by the amines was the basis for evaluating the corrosion inhibition.

The percentage protection was calculated by subtracting from the weight loss of the control the weight loss of the treatment and dividing the result by the control. Correct results based on the experiments are shown in Table II. It will be evident that Table II shows that some materials which were satisfactory in the degradation test were not satisfactory in the corrosion test.

First of all, all of the materials condensed with ethylene oxide which had more than 10 moles of ethylene oxide per mole of amine were unsatisfactory from the standpoint of corrosion, in fact, they were worse than the controls. It is therefore necessary to limit to 10 moles or less of ethylene oxide per mole of amine in order to obtain a product useful from the standpoint of preventing corrosion.

Furthermore, it was found that the condensate with propylene oxide in any concentration at all over the range tested promoted corrosion rather than helped corrosion protection, so that propylene oxide condensate is counterindicated.

It was furthermore found as, for example, in Table II, Experiment 13, that the presence of double bonds does not affect the power to inhibit corrosion to any appreciable extent as compared with the saturated straight chain long chain amines. In this Experiment 13 over 60% of the amine contains one or two double bonds, but this does not seriously affect the corrosion protection.

Table II, Experiment 12, shows that short carbon chain amines containing 8 to 14 carbon atoms in the carbon chain when condensed with only 2 moles of ethylene oxide make the corrosion worse rather than better, and therefore are counterindicated. Accordingly, the lower limit of the amine chain length has been placed at 16 carbon atoms.

All of these tests are short time tests and a concentration of 20 p.p.m. of active ingredient was used in such accelerated tests. As a practical matter, however, this concentration would normally be very expensive and usually a concentration in the range of 0.1 to 10 p.p.m. is employed. The reason for using the high concentration of 20 p.p.m. in the tests was to obtain representative results in the comparatively short time of 20 hours. Since the treatment is one in which a protective film is carried by the flowing stream of the condensate water or steam, and thus deposited on the surface to be protected, it is only necessary to use sufficient treatment to gradually lay such a film. In actual practice, therefore, relatively low concentrations within the range specified are commonly used. There are also factors in actual practice such as the amount of surface to be covered and the possibility of recycling the amine by using return condensate as feed which may vary the minimum feed concentration to produce satisfactory protection. A feed concentration of 0.84 p.p.m. of octadecylamine condensed with 2 moles of ethylene oxide has proved to be very satisfactory in plant application, and based upon my experiments 0.1 p.p.m. is the lowest (as found) reaching concentration which brings reasonable protection under optimum conditions.

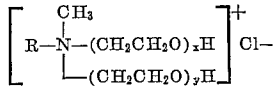
Experiments have been carried out to determine the degradation resistant properties and the corrosion inhibitory properties of these materials under actual operating conditions. Octadecylamine condensed with 2 moles of ethylene oxide was fed into an industrial plant condensate system as a dilute emulsified solution at the rate of 0.84 p.p.m. based on the steam produced. In prior use of octadecylamine at this plant severe degradation of the amine in the condensate system had occurred. In the case, however, of the amine ethylene oxide product as referred to above, the amount of old degradation products formed in the return line system gradually decreased until the problem virtually disappeared. This varified the findings obtained in the laboratory.

The corrosion protection continued to be of the same high order as that obtained by octadecylamine alone.

METHOD OF FEED

The primary straight long chain amines are hard waxy solids and they are difficult to emulsify in water for feeding purposes. The ethylene oxide products above referred to on the other hand are easily prepared by the addition of any one of a number of well known emulsifiers.

One of the most common of these is an ethoxylated quaternary ammonium chloride salt as set forth below:



Formula I

where R is a residue of a fatty acid having a carbon chain length of 10 to 29 and preferably 10 to 24 inclusive, most desirably 10 to 18 inclusive, such as a cocoanut acid residue containing C_{10}, C_{12} and C_{14} mixed fatty acid residues or an oleyl residue or a stearyl residue, and x and y total the mol ratio of polyoxyethylene to R in the molecule and involve a mol ratio of total polyoxyethylene to R of between 5:1 and 15:1. R can be saturated or can contain one double bond in the carbon chain.

These materials are commonly referred to as Ethoquads, and are designated by an initial letter or number, a slant line and a final number such as Ethoquad 18/25. The initial letter or number designates the aliphatic group or groups which compose R as follows:

C=cocoanut acids residue, consisting of C_{10}, C_{12} and C_{14} mixed
O=oleyl residue
18=stearyl residue

The number to the right of the slant line is the total of $x+y-10$ so that Ethoquad 18/25 is of the stearyl series and has a mol ratio of C_2H_4O to R of 15:1.

Typical examples of the Ethoquads are as follows:

Ethoquad C/25
Ethoquad O/15
Ethoquad O/25
Ethoquad 18/15
Ethoquad 18/25

It is preferred to use Ethoquad 18/25 in emulsifying the products of the present invention. The emulsifier can be used in concentrations from 5 to 20% on the dry weight of the amine and is preferably used in a concentration of about 10% on the dry weight of the amine.

SUMMARY

It will be evident that the present invention offers the advantage of preventing degradation of the amine while permitting effective corrosion protection in a flowing steam or condensate line, where the amine straight carbon chain has a length of from 16 to 22 carbons atoms and is condensed with 1 to 10 moles inclusive of ethylene oxide. The amine should be used in a quantity sufficient to coat the interior of the line and preferably in a range between 0.1 and 20 p.p.m. and most desirably in a range between 0.1 and 10 p.p.m.

As shown by Table II, Experiments 6, 7 and 8, the protection is higher with a concentration of ethylene oxide of 1 to 4 moles per mole of amine, is slightly lower with a concentration of 5 moles per mole of amine and the protection is not as good where the concentration is 10 moles of ethylene oxide per mole of amine. Good amines to use are octadecylamine and docosylamine, and preferably in the range of 1 to 4 moles of ethylene oxide although permissibly in the range from 1 to 10 miles of ethylene oxide per mole of amine. Effective corrosion protection may be obtained using docosylamine conthough permissibly in the range from 1 to 10 moles of densed with 10 moles of ethylene oxide, or docosylamine condensed with 5 moles of ethylene oxide or docosylamine condensed with 2 moles of ethylene oxide.

It will be evident that the water systems referred to in connection with the present invention as flowing water systems will typically include such things as condensate return lines, steam lines, dryers and other post boiler equipment of this character which will typically have metal surfaces of steel or of copper base alloys which must be protected against corrosion.

In view of my invention and disclosure, variations and modifications to meet individual whim or particular need will doubtless become evident to others skilled in the art, to obtain all or part of the benefits of my invention without copying the process and composition shown, and I,

therefore, claim all such insofar as they fall within the reasonable spirit and scope of my claims.

Table I.—Degradation tests of amines

No.	Amine	Absorbance at 6.1 Microns—		
		Before heating	After heating	Amount deg.[1]
1	Octadecylamine	0.139	0.230	0.091
2	Secondary Hydrogenated Tallow Amine	0.096	0.122	0.026
3	Secondary Tallow Amine	0.141	0.222	0.081
4	Tertiary methyl dihydrogenated tallow amine	0.118	0.303	0.185
5	Tertiary dimethyl octadecylamine	0.413	0.671	0.258
6	Octadecylamine condensed with 2 moles ethylene oxide adduct	0.041	0.043	0.002
7	Octadecylamine condensed with 5 moles ethylene oxide adduct	0.090	0.093	0.003
8	Octadecylamine condensed with 10 moles ethylene oxide adduct	0.173	0.174	0.001
9	Octadecylamine condensed with 50 moles ethylene oxide adduct	0.054	0.043	−0.011
10	Hydrogenated tallow amine condensed with 2 moles propylene oxide adduct	0.038	0.040	0.002
11	Hydrogenated tallow amine condensed with 15 moles propylene oxide adduct	0.075	0.135	0.060
12	Mixed straight chain primary amines condensed with 5 moles ethylene oxide per mole amine.[2]	0.178	0.192	0.014
13	Mixed straight chain primary amines condensed with 15 moles ethylene oxide per mole amine.[2]	0.222	0.232	0.010
14	Mixed straight chain primary amines condensed with 50 moles ethylene oxide per mole amine.[2]	0.175	0.165	−0.010
15	Mixed straight chain amines, some chains containing double bonds condensed with two moles of ethylene oxide per mole amine.[3]	0.107	0.115	0.008
16	Same as 15 but condensed with 5 moles ethylene oxide per mole of amine	0.210	0.216	0.006
17	Same as 15 but condensed with 15 moles ethylene oxide per mole of amine	0.099	0.100	0.001
18	Mixed straight chain amines [4]	0.024	0.440	0.416
19	Mixed straight chain amines as in 18 condensed with 2 moles ethylene oxide per mole of amine.	0.036	0.066	0.030

[1] The amount degraded is the difference in absorbance units between the intensity of the absorbance, at 6.1 microns, before and after heating. It is therefore a measure of the susceptibility to degradation by heat of the compound measured. The intensity of the absorbance of the carbon to hydrogen bond at 6.8 microns was used as a measure of the thickness of the amine sample in the infrared beam. The absorbance of the amide band at about 6.1 microns was calculated on the basis of a 1.0 absorbance for the 6.8 micron carbon to hydrogen band.
[2] Chain length varied from 8 to 14 with 12 predominating.
[3] Chain lengths were 16 and 18 carbon atoms long.
[4] Chain lengths were 16 to 22 carbon atoms long.

Table II.—Corrosion protection by amines in condensate

No.	Treatment	Mgs. loss	Percent protection
1	None	43.4	0.00
2	Octadecylamine	4.6	89.6
3	Secondary tallow amine	Could not be fed	
4	Tertiary methyl di(Hydrogenated tallow) amine	108.0	−151
5	Tertiary dimethyl octadecylamine	41.4	4.6
6	Octadecylamine condensed with 2 moles ethylene oxide	5.0	88.5
7	Octadecylamine condensed with 5 moles ethylene oxide	12.2	72.0
8	Octadecylamine condensed with 10 moles ethylene oxide	30.2	30.5
9	Octadecylamine condensed with 50 moles ethylene oxide	61.3	−41.4
10	Hydrogenated tallow amine condensed with 2 moles propylene oxide adduct	63.2	−46
11	Hydrogenated tallow amine condensed with 15 moles propylene oxide adduct	99.9	−133
12	Mixed straight chain primary amines condensed with two moles ethylene oxide per mole amine.[1]	55.7	−28.4
13	Mixed straight chain amines, some chains containing double bonds condensed with two moles ethylene oxide per mole amine.[2]	9.7	78
14	Same as 13 but condensed with 50 moles ethylene oxide per mole of amine	51.6	−19
15	Mixed straight chain amines condensed with two moles ethylene oxide per mole of amine.[3]	5.5	87.5

[1] Chain length varied from 8 to 14 carbon atoms with the 12 carbon atoms chain length predominating.
[2] Chain lengths contained 16 and 18 carbon atoms.
[3] Chain lengths varied from 16 to 22 carbon atoms.

Having thus described my invention what I claim as new and desire to secure by Letters Patent is:

1. A process of preventing corrosion in steam and condensate lines forming a flowing water system, which comprises maintaining in the flowing stream of such a water system as effectively the only corrosion inhibitor a dispersion of from 0.1 to 20 p.p.m. of a primary straight chain amine of 16 to 22 carbon atoms chain length condensed with 1 to 10 moles of ethylene oxide, the quantity of corrosion inhibitor being sufficient to form a protective film on the inside of said water system.

2. A process of claim 1, in which the amine is octadecylamine condensed with 10 moles of ethylene oxide and the quantity of said amine in the water system does not exceed 10 p.p.m.

3. A process of claim 1, in which the amine is octadecylamine condensed with 5 moles of ethylene oxide and the quantity of said amine in said water system does not exceed 10 p.p.m.

4. A process of claim 1, in which the amine is octadecylamine condensed with 2 moles of ethylene oxide and the quantity of said amine in said water system does not exceed 10 p.p.m.

5. A process of claim 1, in which the amine is docosylamine condensed with 10 moles of ethylene oxide and the quantity of said amine in said water system does not exceed 10 p.p.m.

6. A process of claim 1, in which the amine is docosylamine condensed with 5 moles of ethylene oxide, and the quantity of said amine in said water system does not exceed 10 p.p.m.

7. A process of claim 1, in which the amine is docosylamine condensed with 2 moles of ethylene oxide and the quantity of said amine in said water system does not exceed 10 p.p.m.

8. A process of claim 1, in which the amine constitutes mixed primary saturated straight carbon chain amines and the quantity of said amine in said water system does not exceed 10 p.p.m.

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